The molybdenum isotopic composition of the modern ocean

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INTRODUCTION

Molybdenum (Mo) has seven naturally occurring stable isotopes (92Mo, 94Mo, 95Mo, 96Mo, 97Mo, 98Mo, and 100Mo; de Laeter et al., 2003). Recent developments in analytical techniques, particularly the advent of multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), have allowed the precise determination of differences in the isotopic composition of Mo between samples and reference standards (Anbar et al., 2001; Siebert et al., 2001; Pietruszka et al., 2006; Nakagawa et al., 2008; Pearce et al., 2009). The reactivity of Mo in aqueous solution is very dependent on redox conditions and coexisting ligands, leading to significant variations in Mo isotopic composition as well as Mo concentrations in natural waters (Bertine, 1972; Helz et al., 1996; Zheng et al., 2000; Vorlicek and Helz, 2002; Helz et al., 2011; Wang et al., 2011). Mo isotopic data are generally reported in the literature in terms of δ100Mo or δ98/95Mo. The value of δ98/95Mo is defined by the following equation

\[ \delta^{98/95}Mo(\%e) = \left( \frac{98^{95}Mo_{\text{sample}}}{98^{95}Mo_{\text{standard}}} - 1 \right) \times 1000 \]  

and is converted to δ98/95Mo by multiplying 0.67 when the system follows mass-dependent fractionation. Though no commonly-used Mo isotopic standard currently exists (see later), the standards used by different laboratories do appear to be isotopically similar at the level of 0.1–2‰. Continental rock samples, such as granite, basalt, and clastic sediments, have δ98/95Mo of ~0.1‰ (Barling et al., 2001; Siebert et al., 2003). Ferromanganese oxides, which scavenger Mo from seawater inoxic conditions, have a light isotopic signature (δ98/95Mo = −1.0 to −0.5‰; (Barling et al., 2001; Siebert et al., 2003), whereas sediments formed in euxinic conditions (aqueous H2S concentrations higher than ~11 µM, the action point pro-
posed by Helz et al. (1996) have a heavy isotopic signature (δ98/95Mo = 2.2 to 2.5‰; Barling et al., 2001; Arnold et al., 2004; Nagler et al., 2005; Neubert et al., 2008). Sediments formed beneath suboxic or anoxic bottom water (Poulson et al., 2006; Siebert et al., 2006; Poulson Brucker et al., 2009; Scheiderich et al., 2010) and carbonates (Voegelin et al., 2009) show variable isotopic compositions between the oxic and euxinic end-members. Besides these field observations, the isotopic fractionation of Mo has been experimentally evaluated for adsorption to manganese (Mn) oxides (Barling and Anbar, 2004; Wasylenki et al., 2008) and to iron (Fe) (oxyhydr)oxides (Goldberg et al., 2009), release from shales (Liermann et al., 2011), and assimilation by cyanobacteria (Zerkle et al., 2011). These results have indicated some potential for Mo isotopes in sediments to be a unique and powerful proxy in geochemical studies of past oceanic euxinia (Barling et al., 2001; Siebert et al., 2003; Archer and Vance, 2008; Poulson Brucker et al., 2009; Pearce et al., 2010b; Kendall et al., 2011), the rise of oxygen on the early Earth (Arnold et al., 2004; Siebert et al., 2005; Wille et al., 2007; Duan et al., 2010; Voegelin et al., 2010), and ocean circulation (Wen et al., 2011).

For accurate interpretation of geological Mo isotopic data, it is crucial to understand the cycle of Mo isotopes in the modern hydrosphere. Although pioneering studies assumed that the Mo input from rivers to the ocean would have a Mo isotopic composition similar to continental rocks (δ98/95Mo ~ 0‰; Siebert et al., 2003), recent studies on river and estuarine water revealed great variations in the isotopic composition of dissolved Mo (δ98/95Mo = –0.1 to 2.3‰; Archer and Vance, 2008; Pearce et al., 2010a; Scheiderich et al., 2010; Neubert et al., 2011). Data on the hydrothermal input are scarce. Low-temperature ridge-flank hydrothermal input is assumed to have an end-member value of δ98/95Mo ~ 0.8‰ based on observations at the Juan de Fuca Ridge (McManus et al., 2002), whereas an extremely light Mo (δ98/95Mo ~ –3.4‰) has been found in hydrothermal waters from Iceland (Pearce et al., 2010a).

Mo isotopic data for seawater are also scarce. Mo is present in oxic seawater predominantly as dissolved MoO₄²⁻ (Bertine, 1972). Mo has a concentration as high as 10⁷ nmol/kg (normalized to a salinity (S) of 35) and is distributed uniformly in the modern oxic ocean with a residence time of ~800 ky (Collier, 1985; Sohrin et al., 1987; Tuit and Ravizza, 2003; Firdaus et al., 2008). Because of this uniformity, it has been implicitly assumed that Mo isotopes are homogeneously distributed in the ocean, with δ98/95Mo of ~2.3‰ on the basis of measure-
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ment of a small number of samples (Barling et al., 2001; Siebert et al., 2003; Arnold et al., 2004; Archer and Vance, 2008). There has been no internationally-certified Mo isotope standard, and each of the above few data were reported relative to different working laboratory standards. In addition, a limited number of Mo isotopes were measured, because most studies employed mass bias correction techniques using elemental doping with zirconium (Zr), which interferes $^{92}$Mo, $^{94}$Mo, and $^{96}$Mo, or using a double-spike made up of $^{97}$Mo and $^{100}$Mo (and the double spike approach assumes mass-dependent fractionation).

We have developed a new analytical method for determining the isotopic composition of dissolved Mo in seawater by employing a chelating resin technique for the preconcentration of Mo and an elemental doping technique using strontium (Sr) for mass bias correction (Nakagawa et al., 2008). This method is simple and rapid enough to allow the processing of a large number of seawater samples. In addition, we can measure every stable Mo isotope with this method. In the previous study (Nakagawa et al., 2008), we reported data on four kinds of seawater samples. In this study, we applied this technique to the isotopic analysis of dissolved Mo in 172 seawater samples obtained from the Pacific, Atlantic, and Southern Oceans. Thus we report for the first time on the global distribution of a full suite of the stable Mo isotopes in seawater. We also report nine full depth-profiles.

MATERIALS AND METHODS

Seawater

Seawater samples were collected from nine stations (Fig. 1). Three stations (K2, KNOT, and 35N) in the western North Pacific were visited during the MR05-01 cruise of the R/V Mirai (JAMSTEC) in March 2005. Two stations (St. 7 and St. 8) in the Philippine Sea were visited during the KH-06-2 cruise of the R/V Hakuho Maru (JAMSTEC) in June 2006. Two stations (SX06 and SX09) in the Southern Ocean and SX18 in the western South Pacific were visited during the KH-04-5 cruise of the R/V Hakuko Maru from December 2004 to January 2005. Station BATS in the eastern North Atlantic was visited for US-GEOTRACES intercalibration activity during the
KN193-5 cruise of the R/V Knorr (Woods Hole Oceanographic Institution) in June 2008. The temperature-salinity (T-S) diagram for all the samples is shown in Fig. 2. Major water masses (Emery, 2001) are labeled on the diagram. Our samples contain seawater from at least ten major water masses in the modern ocean. Among these samples, the lowest dissolved oxygen concentration (of 15.9 umol/kg) was found at 400 m depth at K02.

On board the R/V Mirai and Hakuhou Maru, seawater samples from each depth were collected using Niskin-X sampling bottles (General Oceanics) that were mounted on a carousel sampler equipped with a CTD (Sohrin and Bruland, 2011). On deck, the seawater was transferred to a clean sampling van, A small quantity of the preconcentrated sample solution was diluted and used for the determination of Mo concentrations, [Mo] (nmol/kg), by ICP-atomic emission spectrometry (ICP-AES, Optima 2000 DV, Perkin-Elmer). The calibration line was obtained with working standards prepared from a Mo standard solution (WAKO Pure Chemical Industries). The Mo recovery test from seawater samples was verified quantitative recovery with RSD ~ 5% (Nakagawa et al., 2008).

Mo concentration determination

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RESULTS

Data for δ²⁰⁸⁷⁸⁷Mo (A = 92, 94, 96, 97, 98 and 100) along with T, S and concentrations of oxygen and Mo are summarized in the Appendix table (available at http://www.terrapub.co.jp/journals/OI/archives.html). There were a few outliers for both δ⁸⁷⁹⁵Mo and [Mo]. Since they appeared to occur randomly because of mistakes in analysis, they were removed from the following analysis and discussion. We arbitrarily adopted a ±3SD cut-off, with the result that the rejected outliers made up less than 1.2% of the dataset.

The mean [Mo] was 106 ± 5 nmol/kg (2SD; n = 171). The normalized concentration to S = 35 was 107 ± 7 nmol/kg (n = 168). These values are in good agreement with literature data (Collier, 1985; Sohrin et al., 1987; Tuit and Ravizza, 2003; Firdaus et al., 2008). The results indicate that dissolved Mo in seawater was quantitatively collected by our technique.

The average isotope composition in δ⁸⁷⁹⁵Mo was as follows: δ⁸⁷⁹⁵Mo = -2.54 ± 0.16‰ (2SD; n = 170), δ⁴⁰⁴⁰/⁹⁵Mo = -0.73 ± 0.19‰ (n = 170), δ⁹⁸⁹⁵Mo = 0.85 ± 0.07‰.
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\[ \delta^{92/95}{\text{Mo}} = 1.68 \pm 0.08 \text{‰} \]
\[ \delta^{94/95}{\text{Mo}} = 2.48 \pm 0.10 \text{‰} \]
\[ \delta^{98/95}{\text{Mo}} = 4.07 \pm 0.18 \text{‰} \]

The relatively large SD for \( \delta^{92/95}{\text{Mo}}, \delta^{94/95}{\text{Mo}}, \text{and} \delta^{100/95}{\text{Mo}} \) may be attributed to interference from seawater-derived \( ^{92}\text{Zr}, ^{94}\text{Zr}, \text{and} ^{100}\text{Ru} \), respectively. Vertical profiles of \( \delta^{95}{\text{Mo}} \) and the normalized concentration of Mo at three stations in the North Pacific, Southern, and North Atlantic Oceans are shown in Fig. 3. The profiles of oxygen are also shown for the stations in the North Pacific and Southern Oceans. Every \( \delta^{95}{\text{Mo}} \)
showed uniform profiles at the other six stations as well as the above three stations. There are no significant inter ocean variations. The average and ±2SD of δ97/95Mo and δ98/95Mo for each water mass are plotted in Fig. 4. The SD was relatively large for some water masses, such as PSIW (n = 3), AASW (n = 6), SAASW (n = 4) and AAIW (n = 2). The reason is not clear at present. The averages for each water mass are within the range of the total average ±2SD, suggesting that the formation of water mass does not cause significant mass fractionation among the Mo isotopes.

Redox state is a major factor controlling the fractionation of Mo isotopes, as summarized in the introduction. The values of δA/95Mo are plotted against the oxygen concentration in Fig. 5. The oxygen concentration data were available for 146 samples from the Pacific and Southern Oceans. It is clear that there are no significant variations in δ97/95Mo as a function of the oxygen concentration. The results indicate that oxic fractionation is expected for Mo when the oxygen concentration is higher than 16 µmol/kg.

**DISCUSSION**

**Homogeneity of Mo isotopes in the modern oxic ocean**

We did not observe significant deviations for either the Mo concentration or isotopic composition, within the precisions of our methods (5 nmol/kg for [Mo] and 0.10‰ for δ98/95Mo in 2SD). Poulson Brucker *et al.* (2009) proposed a revised modern marine Mo budget by utilizing Mo isotopic data. According to this model, the global Mo input to the ocean consists of a riverine flux of \( -1.8 \times 10^8 \) mol/y and a low-temperature hydrothermal flux of \( -0.2 \times 10^8 \) mol/y. Three major sinks are proposed. The flux of Mo into oxic Mn-rich sediments is estimated to be \( -0.9 \times 10^3 \) mol/y. The continental margin sink, underling waters that are depleted in free oxygen but with sulfide concentrations below the action point of ~11 µM, has a flux of
The molybdenum isotopic composition of the ocean is estimated to be \(\sim 0.9 \times 10^8\) mol/y. The euxinic sink flux is estimated to be \(\sim 0.1 \times 10^8\) mol/y. Typically, the Mo concentration is conservative against S in estuaries and continental shelves (Head and Burton, 1970; Sohrin et al., 1999). \(\delta^{98/95}\text{Mo}\) is also more-or-less conservative in the two estuaries that have been studied—i.e., \(\delta^{98/95}\text{Mo}\) shows a linear correlation with a reciprocal of Mo concentration \(1/[\text{Mo}]\) (Archer and Vance, 2008; Pearce et al., 2010a). A discharge-weighted global riverine average input flux was estimated to have \([\text{Mo}] = 6\) nmol/kg and \(\delta^{98/95}\text{Mo} = 0.7\%\) (Archer and Vance, 2008). The modern seawater average of \(S = 35\) is estimated to have \([\text{Mo}] = 107\) nmol/kg and \(\delta^{98/95}\text{Mo} = 2.48\%\) on the basis of this study. When we assume Mo is completely conservative with S throughout the oxic ocean, the following equations would be valid:

\[
[\text{Mo}] = 2.89 \times S + 6 \quad (2)
\]

\[
\delta^{98/95}\text{Mo} = -11.27 \times 1/[\text{Mo}] + 2.59. \quad (3)
\]

In our data, \(S\) varies from 33.052 to 36.727, which should result in variations in \([\text{Mo}]\) from 102 to 112 nmol/kg and of \(\delta^{98/95}\text{Mo}\) from 2.48 to 2.49\%. However, no significant correlations were observed between \([\text{Mo}]\) and \(S\) or between \(\delta^{98/95}\text{Mo}\) and \(1/[\text{Mo}]\). There are two possible explanations. One explanation is due to insufficient precisions in our analytical methods for \([\text{Mo}]\) and \(\delta^{98/95}\text{Mo}\). Another possibility is that small and real deviations from conservative behavior actually exist for Mo.

Non-conservative signatures have actually been observed for dissolved Mo concentrations in estuarine and coastal waters (Dellwig et al., 2007; Rahaman et al., 2010) and in the eastern tropical Pacific (Tuit and Ravizza, 2003). The non-conservative signatures also reported for \(\delta^{98/95}\text{Mo}\) in the low salinity zone of an estuary (Pearce et al., 2010a). Possible mechanisms for non-conservative behavior of dissolved Mo in oxic seawater are uptake by phytoplankton and cyanobacteria, remineralization from biogenic particles, adsorption to Mn–Fe (oxyhydr)oxides, and reductive release from Mn–Fe (oxyhydr)oxides. Improvement in analytical methods and further observations are necessary to address the issue.

Mass-dependent isotope fractionation of Mo in the modern ocean

The total average values of \(\delta^{98/95}\text{Mo}\) are a strong linear function of the atomic mass. The regression line is \(\delta^{98/95}\text{Mo} = 0.8220 \times m - 78.00\) \((R^2 = 0.999, \ SE = 0.07)\). The values of \(\delta^{97/95}\text{Mo}\) are plotted against those of \(\delta^{98/95}\text{Mo}\) in Fig. 6. The slope of the regression line passing through the origin is 0.674 for equilibrium fractionation and 0.675 for kinetic fractionation using a molecular moiety of Mo–O for calculating \(m^*\). The observed slope is analytically identical to these values. Every plot between \(\delta^{97/95}\text{Mo}\) and \(\delta^{98/95}\text{Mo}\) gives similar results, though the correlations are never strong \((R^2 = 0.175–0.735)\) because of narrow ranges in \(\delta^{98/95}\text{Mo}\).

These results demonstrate for the first time, on the basis of a number of actual measurements, that the stable isotopes of dissolved Mo in the modern oxic ocean follow a mass-dependent fractionation law. It is most likely...
Table 1. Mo isotopic composition in the modern oxic seawater

<table>
<thead>
<tr>
<th>Ocean</th>
<th>Station or identity</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Depths (m)</th>
<th>Mo speciation</th>
<th>$\delta^{97/95}Mo^{*}$ 2SD</th>
<th>$\delta^{98/95}Mo^{*}$ 2SD</th>
<th>Concentration (nmol/kg)</th>
<th>2SD</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Pacific</td>
<td>CTD-52</td>
<td>104.367°W</td>
<td>9.767°N</td>
<td>105</td>
<td>Dissolved</td>
<td>1</td>
<td>1.48</td>
<td>2.4</td>
<td>115</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>Suruga Bay</td>
<td>138.32°E</td>
<td>34.85°N</td>
<td>687</td>
<td>Dissolved</td>
<td>13</td>
<td>1.67 (1.59)</td>
<td>0.09</td>
<td>2.47 (2.35)</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>SAFI S1</td>
<td>140°W</td>
<td>30°N</td>
<td>0</td>
<td>Dissolved</td>
<td>3</td>
<td>1.62 (1.54)</td>
<td>0.07</td>
<td>2.37 (2.25)</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>SAFI D2</td>
<td>140°W</td>
<td>30°N</td>
<td>1000</td>
<td>Dissolved</td>
<td>2</td>
<td>1.68 (1.57)</td>
<td>0.05</td>
<td>2.49 (2.37)</td>
<td>0.09</td>
</tr>
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<td></td>
<td>KO2</td>
<td>100.005°E</td>
<td>47.023°N</td>
<td>5-51.33</td>
<td>Dissolved</td>
<td>20</td>
<td>1.69 (1.61)</td>
<td>0.07</td>
<td>2.48 (2.36)</td>
<td>0.09</td>
</tr>
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<td></td>
<td>KNOT</td>
<td>155.002°E</td>
<td>44.003°N</td>
<td>5-52.64</td>
<td>Dissolved</td>
<td>23</td>
<td>1.67 (1.59)</td>
<td>0.06</td>
<td>2.48 (2.36)</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>3SN</td>
<td>159.999°E</td>
<td>34.998°N</td>
<td>11-45.00</td>
<td>Dissolved</td>
<td>20</td>
<td>1.68 (1.60)</td>
<td>0.07</td>
<td>2.48 (2.36)</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>St. 8</td>
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<td>20.000°N</td>
<td>5-39.25</td>
<td>Dissolved</td>
<td>19</td>
<td>1.65 (1.57)</td>
<td>0.06</td>
<td>2.44 (2.33)</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>St. 7</td>
<td>128.001°E</td>
<td>15.000°N</td>
<td>5-39.27</td>
<td>Dissolved</td>
<td>21</td>
<td>1.66 (1.58)</td>
<td>0.05</td>
<td>2.47 (2.35)</td>
<td>0.08</td>
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<tr>
<td></td>
<td>SX18</td>
<td>169.999°W</td>
<td>39.998°S</td>
<td>5-45.79</td>
<td>Dissolved</td>
<td>21</td>
<td>1.70 (1.62)</td>
<td>0.1</td>
<td>2.52 (2.40)</td>
<td>0.12</td>
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<td>Atlantic</td>
<td>IAPSO standard</td>
<td>Dissolved</td>
<td>2.3</td>
<td></td>
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<td></td>
<td>115</td>
<td>115</td>
<td>Siebert et al. (2008)</td>
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<td></td>
<td>IAPSO standard</td>
<td>Dissolved</td>
<td>2.41</td>
<td>0.05</td>
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<td>121</td>
<td>Siebert et al. (2008)</td>
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<td>CASS-4</td>
<td>Dissolved</td>
<td>2.23</td>
<td>0.09</td>
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<td></td>
<td></td>
<td>92.1</td>
<td>92.1</td>
<td>Schreuder et al. (2010)</td>
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<td></td>
<td>NASS-5</td>
<td>Dissolved</td>
<td>4</td>
<td>1.64 (1.60)</td>
<td>0.08</td>
<td>2.47 (2.35)</td>
<td>0.10</td>
<td>90</td>
<td>1</td>
<td>Nakagawa et al. (2008)</td>
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<td></td>
<td>ARI-1, coast</td>
<td>1</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>115</td>
<td>115</td>
<td>Siebert et al. (2008)</td>
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<tr>
<td></td>
<td>Labrador Sea, FvB</td>
<td>2400</td>
<td>1</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td>115</td>
<td>115</td>
<td>Siebert et al. (2008)</td>
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<tr>
<td></td>
<td>Batsfjord/Barents Sea, C11</td>
<td>22.149°W</td>
<td>64.434°N</td>
<td>1</td>
<td>Dissolved</td>
<td>4</td>
<td>1.67 (1.59)</td>
<td>0.07</td>
<td>2.48 (2.36)</td>
<td>0.07</td>
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<tr>
<td>Southern</td>
<td>SX06</td>
<td>149.976°E</td>
<td>59.999°S</td>
<td>3-3161</td>
<td>Dissolved</td>
<td>18</td>
<td>1.69 (1.62)</td>
<td>0.07</td>
<td>2.51 (2.40)</td>
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<td></td>
<td>SX09</td>
<td>174.155°E</td>
<td>65.146°S</td>
<td>4-3237</td>
<td>Dissolved</td>
<td>17</td>
<td>1.69 (1.61)</td>
<td>0.09</td>
<td>2.50 (2.38)</td>
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<tr>
<td>Indian</td>
<td>CTD-24</td>
<td>1</td>
<td>2.3</td>
<td></td>
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<td></td>
<td>115</td>
<td>115</td>
<td>Siebert et al. (2008)</td>
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</table>

*The values of Nakagawa et al. (2008) and this study were measured relative to a Johnson Matthey Mo standard solution. The values in parentheses are corrected and expressed relative to the CPI Mo ICPMS standard that was used in Archer and Vance (2008).
that this fractionation occurs in oxic sediments during adsorption to Mn oxides (Barling and Anbar, 2004; Wasylenki et al., 2008; Goldberg et al., 2009; Poulson Brucker et al., 2009). In addition, these results confirm the accuracy of our method and the precision of our results.

Synthesis of Mo isotopic data in the modern ocean

All the data for the isotopic composition of dissolved Mo in seawater from the literature and this study are summarized in Table 1. All the values of δ⁹⁶/⁹⁵Mo in Nakagawa et al. (2008) and this work are expressed relative to working standards that were prepared from the same lot of a Johnson Matthey Specpure Mo plasma standard solution. The resulting averages for each station converge in a narrow range: from 1.62 to 1.70 in δ⁹⁶/⁹⁵Mo, and from 2.37 to 2.50 in δ⁹⁸/⁹⁵Mo, whereas these values are relatively high compared to some literature values. We have compared the δ⁹⁰Mo/⁹⁵Mo ratio between the standard used in this work and the CPI Mo ICPMS standard that was used in Archer and Vance (2008). Mo isotopic analysis revealed that δ⁹⁰⁵Mo of the standard in this study was -0.117 ± 0.009‰ (mean and 2SD of 5 different mixtures of the IM standard with double spike) relative to the CPI Mo ICPMS standard. The values in parentheses in Table 1 represent the δ⁹⁵Mo of our seawater samples expressed relative to the CPI Mo ICPMS standard. The corrected δ⁹⁵Mo show better agreement with some data, including that in Archer and Vance (2008). These results indicate that an internationally-certified Mo isotope standard is necessary for a sounder basis for the Mo isotopic composition in the ocean.

Lack of a common standard and reference material is a major problem in Mo isotope geochemistry (Hannah et al., 2007). Recently, Wen et al. (2010) compared the isotopic composition of Mo standard solutions and proposed the NIST 3134 Mo solution as a new candidate for a reference material to report Mo isotopic composition of natural samples. On the other hand, Siebert et al. (2003) proposed mean ocean water Mo (MOMO) as the reference for Mo isotopic composition. This proposal has not been widely adopted, probably because of the effort involved in preconcentration and separation of Mo from seawater. However, our data further confirm the homogeneous isotopic composition of Mo in the ocean and recalls the possibility of using seawater as a reference material for Mo isotopic composition. The advantage of this reference material is that the ocean is one of the largest reservoirs on the Earth and that the variations in isotope composition of Mo are as low as ~0.1‰.

CONCLUSIONS

This study reports the full-depth distributions of every stable isotope of dissolved Mo in the modern oxic ocean for the first time. Each δ⁹⁵Mo converges on a single global average, with 2SD less than 0.19‰. The average (relative to a Johnson Matthey Mo standard solution) and 2SD were as follows: δ²⁹⁶Mo = -2.54 ± 0.16‰, δ⁹⁵⁵Mo = -0.73 ± 0.19‰, δ⁹⁰⁵Mo = 0.85 ± 0.07‰, δ⁹⁸⁵Mo = 1.68 ± 0.08‰, δ⁹⁷⁵Mo = 2.48 ± 0.16‰, and δ⁹⁰⁰⁵Mo = 4.07 ± 0.18‰. The modern oxic ocean is homogeneous in Mo isotope composition as well as in the Mo concentration, and any deviations are at a level less than the analytical uncertainty of the present technique. The first mass fractionation curve and three isotope plots for global seawater samples demonstrate the mass-dependent nature of Mo isotope fractionation in the modern oxic ocean. These results strongly support the possibility of seawater as an international reference material for Mo isotopic composition.

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